

THEORETICAL AND EXPERIMENTAL
STUDIES
IN
NUCLEAR
MAGNETIC RELAXATION

BY
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NUCLEAR MAGNETIC RESONANCE

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THEORETICAL AND EXPERIMENTAL STUDIES IN NUCLEAR MAGNETIC RELAXATION.

INTRODUCTION

Applications of nuclear magnetic resonance spectroscopy to the study of chemical systems have been steadily growing during the last twenty years. Depending on how the magnetic resonance experiment is performed information can be obtained on a variety of parameters characteristic of the system under study. These parameters can schematically be divided into static and dynamic ones. Static parameters occur in the time independent spin hamiltonian that determines positions and intensities of the various resonance lines in the NMR-spectrum. Well-known examples of static parameters are chemical shifts and scalar spin-spin couplings. The dynamic parameters, on the other hand, are determined by the time dependent terms in the hamiltonian. A typical dynamical parameter is the longitudinal relaxation time, T_1 .

There exists a number of simple empirical and semi-empirical rules for the interpretation of chemical shifts and scalar couplings in terms of the chemical structure of a molecule. These rules are based on a large amount of accumulated reference data. Therefore, in identifying an unknown substance, it is of great help to measure chemical shifts and coupling constants.

If, on the other hand, the interest is concentrated on the behaviour of a known substance in a particular sys-

tem, it is often more fruitful to study nuclear magnetic relaxation times T_1 or T_2 . The interpretation of these relaxation times can, though usually not, be made in an empirical way. Instead a theoretical analysis of the relaxation process has to be performed. This illustrates both the strength and the weakness of measuring relaxation times. They are very sensitive to changes in the system but they are also difficult to interpret since they depend on several factors which are not easy to separate.

The present work gives a summary of eight articles, in the following denoted by their roman numbers

I. A bromine-79 nuclear magnetic resonance study of the structure of aqueous solutions of mono-, di-, and tri-alkylammonium bromides.

B. Lindman, H. Wennerström, and S. Forsén, J. Phys. Chem. 74, 754 (1970).

II. The interaction of halide ions with organic cations containing charged nitrogen, phosphorus, or sulfur in aqueous solutions studied by nuclear quadrupole relaxation.

H. Wennerström, B. Lindman, and S. Forsén, J. Phys. Chem. 75, 2936 (1971).

III. Ion binding in liquid crystals studied by NMR. II. ^{35}Cl second order quadrupole interactions in a lamellar mesophase.

G. Lindblom, H. Wennerström, and B. Lindman, Chem. Phys. Lett. 8, 489 (1971).

IV. Proton nuclear magnetic resonance lineshapes in lamellar liquid crystals.

H.Wennerström, Chem. Phys. Lett. 18, 41 (1973).

V. Counter-ion dependent water and amphiphile orientation and deuterium exchange in lyotropic mesophases.

N-O. Persson, H.Wennerström, and B.Lindman, Acta Chem. Scand. 27, 1667 (1973).

VI. Double quantum transitions in deuterium NMR spectra of lyotropic liquid crystals.

H.Wennerström, N-O. Persson, and B.Lindman, J. Magn. Reson. (1974). In press.

VII. Theoretical aspects of the NMR of quadrupolar ionic nuclei in micellar solutions and amphiphilic liquid crystals.

H.Wennerström, G.Lindblom, and B.Lindman, Chemica Scripta (1974). In press.

VIII. Nuclear magnetic relaxation induced by chemical exchange.

H.Wennerström, Molec. Phys. 24, 69 (1972).

These articles concern three different but interrelated topics.

a) The quadrupole relaxation of halogen ionic nuclei in aqueous solutions containing organic cations (I-II).

b) Nuclear magnetic resonance lineshapes in amphiphile-water systems (III-VII).

c) Nuclear magnetic relaxation induced by chemical exchange (VIII).

These three topics will now be discussed separately.

RELAXATION OF HALOGEN IONIC NUCLEI IN AQUEOUS SOLUTIONS
CONTAINING ORGANIC CATIONS.

The nuclei ^{35}Cl , ^{79}Br , ^{81}Br and ^{127}I all possess quadrupole moments. The dominant relaxation mechanism, for such nuclei is usually given by the interaction between the quadrupole moment and the electrical field gradients. In the limit when the correlation time is short compared to the inverse of the nuclear Larmor frequency ω_0 the relaxation rates are given by (1)

$$1/T_1 = 1/T_2 = (3/40)(2I+3)/\{I^2(2I-1)\}(e^2Qq/\hbar)^2(1+\eta^2/3)\tau_c \quad [1]$$

I is the nuclear spin quantum number, eQ the nuclear quadrupole moment, $eq = \frac{\partial^2 V}{\partial z^2}$ is the largest principal component of the electrical field gradient tensor at the nucleus, η is the asymmetry parameter and τ_c the correlation time. For a given nucleus, the relaxation rate is primarily determined by the electrical field gradient and by the correlation time.

For a free halide ion the electrical field gradients are zero due to the spherical symmetry of the ion; likewise for an octahedral or tetrahedral environment of the ion the field gradient vanishes by symmetry. It is thus only a more unsymmetrical hydration of halide ions that will give contributions to the relaxation rate. These contributions are comparatively small and potentially very sensitive to complex formation and other changes in the solution.

In 1968 it was found by Lindman et.al. (2) that the relaxation of ^{79}Br in aqueous solutions of quaternary ammonium bromides was unusually efficient. This observa-

tion was interpreted in terms of an incorporation of some of the bromide ions into a clathrate-like water structure surrounding the alkyl chains. The electrical field gradient was expected to be large in such a site and this explained the observed increase in the relaxation rate.

The experimental investigations reported in papers I and II were performed to further test the assumptions of ref.2 and to get a more complete understanding of the increased relaxation rate. The main results of the investigations can be summarized as

- a) For all alkyl ammonium bromides the relaxation rate increases with increasing number of carbon chains, with increasing chain length and with increasing concentration.
- b) The apparent energy of activation for the relaxation process increases with increasing number of substituents.
- c) There is a dramatic increase in relaxation rate in the monoalkyl ammonium bromide solutions at the critical micelle concentration.
- d) The typical increase in relaxation rate occurs not only for bromine but also for chlorine and iodine.
- e) The increase in the relaxation rate is observed for solutions containing a number of different types of organic cations. For cations having polar groups the increase is less marked.
- f) For one case it was observed that even an uncharged organic molecule could give an increased bromine relaxation rate in aqueous solutions.
- g) No competitive effect between the halide ions was found.

The results summarized in a, d and e give strong support for the original interpretation given in ref. 2. It is interesting to note that the charge on the organic moiety does not seem to be a crucial factor as indicated by f. The abrupt increase in relaxation rate at the critical micelle concentration (CMC) was first found by Eriksson et.al. (3) and has subsequently been used in Lund to determine CMCs and to investigate the ion binding to the micelle surface.

The problems treated in ref. 2 and in papers I and II have recently been reconsidered by Hertz and Holz (4). These authors have extended the experimental investigations and have given a more detailed theoretical analysis of the relaxation process. Hertz and co-workers have, during a range of years, made a thorough investigation of the nuclear magnetic relaxation in electrolyte solutions (5-8). With the results of these papers as a basis, Hertz and Holz present a model for the halogen relaxation in aqueous solutions containing organic molecules or ions. Their basic assumption is that the presence of the organic solute induces an asymmetry in the hydration of the halide ion, which in turn gives large field gradients and short relaxation times. They conclude that it is the hydrophobic hydration of the alkyl chains that is causing the unsymmetrical hydration. Since hydrophobic hydration essentially gives the clathrate-like water structure around the alkyl chains it follows that the interpre-

tation made by Hertz and Holz have much in common with the one presented in ref. 2 and in papers I and II. The main difference is that Hertz and Holz assume a uniform distribution of the ions in the solution which implies that there is no binding of the halide ions to the clathrate-like water. It is indeed difficult to explain the linear dependence of the relaxation rate on the concentration up to one molal in alkyl ammonium salt solutions, if there is an appreciable binding of the anion to the hydration water of the cation (4). On the other hand, the marked difference between cationic, neutral and anionic species in their effect on halide relaxation seems to favour the assumption of a weak anion-cation association. Ion pairing in aqueous solutions of tetraalkyl ammonium halides has also been inferred from other experimental studies (9).

NUCLEAR MAGNETIC RESONANCE LINESHAPES IN LYOTROPIC LIQUID CRYSTALS.

Liquid crystals

When an amphiphile like dodecyltrimethyl ammonium chloride, DOTAC, is mixed with water a number of different liquid crystalline phases can be formed depending on the amphiphile to water proportions. In all these liquid crystalline phases the DOTAC⁺ cations form large aggregates with the charged endgroups on its surfaces. The shape and the packing of these aggregates differ from phase to phase. In the hexagonal phase the DOTAC⁺ anions form rod-shaped cylinders, which are packed in an

hexagonal array. In the lamellar phase, on the other hand, the anions form planar bilayers which are separated by water sheets.

Liquid crystalline phases of these and similar types are formed by a large number of amphiphile-water systems. Examples of such systems are $\text{H}_2\text{O}-\text{C}_n\text{H}_{2n+1}\text{COO}^-\text{M}^+$; $\text{H}_2\text{O}-\text{C}_n\text{H}_{2n+1}\text{N}^+(\text{CH}_3)_3\text{X}^-$; H_2O -lecithin (M^+ is an alkali ion and X^- a halide ion, and $n > 6$ approximately). For some of these systems addition of an alcohol or a carboxylic acid gives rise to new liquid crystalline phases. Lyotropic liquid crystalline phases are potentially very interesting systems. A biological membrane is, for example, analogous to lamellar liquid crystals.

Nuclear magnetic resonance is one useful experimental method in the investigation of liquid crystals. One advantage with the NMR method is that it is possible to investigate the properties of both amphiphile, water and counterion. The papers III-VII give contributions to the study of all the three different types of species. These papers are all parts in an investigation of liquid crystalline systems by NMR methods, being performed at the Division of Physical Chemistry 2 in Lund.

NMR in liquid crystals

In nuclear magnetic resonance investigations of lyotropic liquid crystals there is one point which is necessary to understand before a correct interpretation of the experimental data is possible. In an isotropic solution the Zeeman interaction and the scalar

spin-spin interaction determine the positions of the lines in the NMR absorption spectrum, while the dipole-dipole and the quadrupole interactions only give relaxation effects. This is no longer true for an anisotropic medium, e.g. a liquid crystal. The reason for this will now be discussed.

The hamiltonian representing a general interaction between a spin system and the surrounding (lattice) can be written as a scalar contraction of spherical tensor operators (10)

$$H = \sum_q (-1)^q F_{-q}^k A_q^k \quad [2],$$

where A_q^k is a standard component of a tensor operator of rank k working on spin variables. F_{-q}^k is a corresponding operator working on lattice variables. The hamiltonian is a scalar and eq. [2] is consequently independent of the coordinate system. In the total spin hamiltonian the Zeeman term is normally dominant and it is convenient to express the spin operators in a laboratory fixed coordinate system. The lattice operators are, for a large number of cases, constants in a molecular fixed coordinate system and are therefore best expressed in this system. The advantage of using standard components of spherical tensors is that their transformation properties have been worked out. Equation [2] can be transformed into (VII)

$$H = \sum_{qq'} (-1)^q F_{-q}^M A_q^L D_{q'-q}^k(\Omega_{LM}) \quad [3].$$

The superscripts M and L denote the molecular and

laboratory coordinate systems respectively. $D_{q'q}^k(\Omega_{LM})$ is the $q'q$ matrix element in the k :th irreducible representation of the full rotation group. The eulerian angles (10) that specify the rotation from the molecular to the laboratory coordinate system are denoted by Ω_{LM} . The orientation of the molecule relative to the magnetic field, and consequently Ω_{LM} , changes with the molecular motion. It is only the mean value of the hamiltonian in eq. [3] that contributes to the static spin hamiltonian. The mean value of eq. [3] is

$$\bar{H} = \sum_{q,q'} (-1)^q F_{-q}^M A_q^L \overline{D_{q'q}^k(\Omega_{LM})} \quad [4].$$

In an isotropic solution all directions Ω_{LM} are equally probable and one obtains (10)

$$\overline{D_{q'q}^k(\Omega_{LM})} = (1/8\pi^2) \int D_{q'q}^k(\Omega_{LM}) d\Omega_{LM} = \delta_{k,0} / (2k+1) \quad [5],$$

which shows that only scalar ($k=0$) intramolecular interactions have non-zero mean values in isotropic solutions. This conclusion can be extended to intermolecular interactions but it is of course not valid for the Zeeman interaction.

In liquid crystals all Ω_{LM} are not equally probable and the mean values $\overline{D_{q'q}^k(\Omega_{LM})}$ are no longer necessarily zero for any k . The dipole-dipole and the quadrupole interactions are represented by second rank tensors ($k=2$) and they can consequently give contributions to the static hamiltonian in liquid crystals but not in isotropic solutions. This is a key point in NMR investigations of liquid crystals.

NMR lineshapes of the protons in the alkyl chains

In a pioneering work on proton resonance in lyotropic liquid crystals Lawson and Flautt (11) observed that the ^1H spectrum of the aliphatic chains of the amphiphile in a lamellar phase showed a peculiar lineshape. They obtained a sharp peak with unusually intense wings. The sharp peak in the centre resembled peaks obtained for isotropic solutions while the wings had a shape more typical for solid samples. Lawson and Flautt gave the name "super lorentzian" to the lineshape and interpreted it as being due to a distribution of correlation times along the aliphatic chains. This view was later questioned by several authors. Hansen and Lawson (12) and Kaufman et.al. (13) suggested that the lineshape was due to local field inhomogeneities. Charvolin and Rigny (14) showed that part of the free induction decay was caused by static dipole interactions and concluded that both "liquid-like" and "solid-like" protons were present. Chan et.al. (15,16) also concluded that static dipole interactions were present and that the sharp peak was due to methyl groups, which were rotating around an axis that formed an angle of about 55° with the magnetic field.

In paper IV it is shown that it is possible to predict a proton resonance lineshape from a few assumptions that have independent experimental justification. These assumptions are

- i) Intermolecular dipole-dipole interactions average to zero.

- ii) The molecular motion is sufficiently fast relative to the inverse of the dipole-dipole interactions to give the lamellae an effective cylindrical symmetry.
- iii) The lamellae are randomly oriented.
- iv) The NMR signal has a substantial intensity at the Larmor frequency for any given orientation of the lamellae.
- v) The shift differences are negligible compared to the dipole-dipole couplings.

It follows from these assumptions that the NMR spectrum of the protons in the alkyl chains should have the typical "super lorentzian" characteristics. In a refinement of the experiments reported in ref. 14 Charvolin and Rigny (17) showed that static dipolar couplings were important also for the narrow part of the proton signal in accordance with the conclusions made in paper IV.

The information that can be obtained from a "super lorentzian" spectrum is rather limited. If it is assumed that one has a gaussian lineshape for a given orientation of a lamella, then the observed spectrum can be used to determine the width of the gaussian curve. The mere existence of a "super lorentzian" lineshape implies that the assumptions i) and ii) are correct, which can give non-trivial conclusions in many cases. Thus, in the lamellar phase in the lecithin-water system a "super lorentzian" lineshape is observed, while the gel phase gives a proton spectrum corresponding to those normally found for solids (18). From second moment

measurements (19), it has been shown that in the gel phase there is a fast rotation around the carbon backbone making assumption ii) valid. From the NMR point of view it then seems clear that the main difference between the liquid crystalline and the gel phase is that the intermolecular dipole-dipole interactions average to zero in the liquid crystalline but not in the gel phase. This implies that the lateral diffusion coefficient is greater than approximately $10^{-14} \text{ m}^2/\text{s}$ in the liquid crystal while it is smaller than this value in the gel phase.

Deuteron magnetic resonance investigations

Deuteron magnetic resonance provides a powerful and experimentally relatively simple method for studying the interaction between (heavy) water and amphiphile in lyotropic liquid crystals. Usually the deuteron signal is split into a doublet in the anisotropic medium. Even when there is a random distribution of, for example, lamellae directions two distinct peaks are obtained in the deuteron NMR spectrum. The average coupling can be calculated from the separation of these peaks. By varying composition, temperature or counterion, changes in the water-amphiphile interaction can be deduced from changes in the quadrupole splitting (20,21,V).

One complication in the interpretation of deuteron splittings is that the amphiphiles often contain hydroxyl or amine protons, which can exchange with the

water deuterons. The appearance of the deuteron spectrum then depends on the rate of exchange of the deuterons between water and amphiphile and on the quadrupole couplings in the two deuteron sites. In the limit of very slow exchange one obtains two doublets with the splittings

$$\Delta_i = |(\nu_Q S)_i| \quad [6],$$

where S is the order parameter (V) and ν_Q is three halves times the quadrupole coupling constant. In the fast exchange case only a single doublet is observed. The splitting is then given by

$$\Delta = |p_1(\nu_Q S)_1 + p_2(\nu_Q S)_2| \quad [7],$$

where p_i gives the relative populations in the two sites. One should note that the contributions from the two sites are summed algebraically in eq. [7]. This is of importance since S can have either sign. Geometric considerations often give the sign of S for hydroxyl and amine deuterons; in such cases one can obtain the sign of S for the water deuterons through eq. [7]. This gives a crude measure of the orientation of the water molecules relative to the amphiphile surface.

As described in paper V the deuteron spectra of the lamellar phase of the system $D_2O-C_7H_{15}COO^-M^+-C_{10}H_{21}OH$ show a marked broadening above room temperature. This was interpreted as being due to chemical exchange between water and decanol deuterons. It was possible to observe the water and decanol signals separately for lower temperatures in accordance with eq. [6]. Above ca. $60^\circ C$, the exchange becomes fast enough for

eq. [7] to be valid.

Chemical exchange effects, occurring between the regions where eqs. [6] and [7] are valid, are well-known in proton NMR and qualitatively the effect is the same in deutron resonance. The main difference between the two cases is that the sites differ in their quadrupole coupling for the deuterons while in proton resonance one usually has a difference in chemical shifts. A further difference between the case considered in paper V and the common proton case is that the spectrum is due to a superposition over all orientations for an unoriented liquid crystalline sample. This has the effect that the chemical exchange broadening appears much less distinct.

In paper V it was shown that it is possible to get a quantitative rationalization of the chemical exchange effects by considering the deutron transitions $m=1 \rightarrow m=0$ and $m=0 \rightarrow m=-1$ separately (m is the magnetic quantum number). Lineshape equations derived for nuclei with spin one half can be applied directly with this assumption. From a comparison between calculated and experimental spectra exchange times are then obtained. The accuracy of such a determination is, however, considerably lower for the case with deutron quadrupole splittings than in proton resonance. The two methods cover, though, different ranges of exchange rates. Deutron quadrupole couplings are usually of the order of 1-30 kHz in liquid crystals and exchange times down to 10 μ s can be determined in favourable cases. With this

deuteron resonance technique one has the possibility to study reactions that can not be studied by proton resonance.

The appearance of an extra central peak in a deuteron spectrum from a liquid crystal has usually been interpreted in terms of water moving isotropically (11,22). If both a quadrupole splitting and a central peak is observed this is an indication of a two phase system. It was however found by Charvolin and Rigny (22,23) and at our laboratory that a weak central peak is observed in spite of the fact that the sample preparation is made carefully to avoid a two phase system.

It occurred to us that a proper explanation of the appearance of a central peak could be that it is due to double quantum transitions. By experimentally investigating the dependence of the various peak intensities on the amplitude of the radio frequency field we obtained strong support for this hypothesis. Further support was obtained from a theoretical analysis based on the equations derived by Yatsiv (24). Both the observed lineshapes and the observed intensities and widths of the central peak agreed well with the theoretical predictions for double quantum transitions.

A typical feature of these spectra is that the double quantum transitions seem unexpectedly intense. This is due to the fact that the double quantum transitions occur at a single frequency, while the single quantum transitions are spread over a wide frequency

range. The integrated intensity of the single quantum transition is, however, much larger than for the double quantum transition. For an oriented sample the quadrupole splitting gives two sharp peaks and observable double quantum transitions are expected only for very strong radio frequency fields.

Alkali and halide ion NMR

It has been observed by several techniques that counterions play an important role in ionic amphiphile-water systems. When the amphiphile forms large aggregates the counterions are bound to the charged surface in order to reduce the electrostatic repulsion between the amphiphile ions. One effect of the counterions is that they can effect phase equilibria significantly in some cases. A group at the Division of Physical Chemistry 2 has in a series of papers (e.g. 25-30) investigated the behaviour of the counterions in amphiphile-water systems using different NMR methods. These studies have given interesting and unique information on the binding of ions to the charged aggregates.

During an attempt to measure the ^{35}Cl relaxation rates in the lamellar phase of the system water-octylammonium chloride G. Lindblom observed an anomalous lineshape of the ^{35}Cl nuclear magnetic resonance. It occurred to us that this lineshape was due to a second order quadrupole interaction. This was confirmed by comparing theoretically calculated and experimentally observed spectra, by studying the field dependence of

the lineshape and by comparing ^{35}Cl and ^{37}Cl spectra of the same sample (III).

This was the first observation of a quadrupolar splitting of ionic nuclei in lyotropic liquid crystals. It was soon shown that quadrupole splittings of ionic nuclei could be observed in a number of liquid crystalline systems (26,29). The observed splittings contain interesting information on the ion binding to the charged amphiphile surface but it has not been possible to obtain a quantitative interpretation of the splittings. It is, in particular, difficult to determine the exact cause of the field gradients at the nucleus.

It has been shown in a number of investigations (e.g. 25,31) that it is possible to interpret relaxation rates of the counterions in a qualitative way. It is even more difficult to get a quantitative description of the relaxation rates than of quadrupole splittings. One has not only to determine the cause of the field gradients but additionally the magnitude of the correlation time. It is furthermore possible that several different motional processes are important in determining the relaxation rate.

The theoretical considerations presented in paper VII were performed to provide a basis for a more quantitative analysis of observed quadrupole splittings and relaxation rates for alkali and halogen ionic nuclei. Expressions for quadrupole splittings and relaxation rates were developed for different models. These equations were then used in order of mag-

nitude calculations of the various observables. The order of magnitude estimates show that it is possible to describe the quadrupole interaction within an electrostatic model, which is of great help in the interpretation of the experimental data.

An interesting result of the derivations of the relaxation rates is that T_1 should be highly orientation dependent when the dominant contribution to the relaxation of an ionic nuclei comes from the exchange between ions that are bound and free ions. This can be tested experimentally by measuring T_1 for an oriented sample of a liquid crystal.

The derivations presented in paper VII are, for a number of important cases, applicable to NMR investigations of amphiphile-water systems and other liquid crystalline phases using nuclei such as ^1H and ^2H . It appears that paper VII contains the first consistent treatment of nuclear magnetic relaxation in liquid crystals where the anisotropy of the system is taken into account. Another result of general interest is that in isotropic solutions, like a micellar solution, one has to distinguish between local anisotropic motions and motions that occur over the dimensions of the micelles. It seems that the contributions to the relaxation rate from the two types of motions are of the same order of magnitude for a number of different systems.

Nuclear magnetic relaxation induced by chemical exchange

Chemical exchange can influence nuclear magnetic relaxation times in a number of ways depending on the rate of exchange. If the exchange is very slow compared to the relaxation rates the signals from the nuclei in the different sites can be observed independently and one obtains distinct relaxation times for each site. If, on the other hand, the exchange is fast compared to the relaxation rates, these should be interpreted as mean values over the sites. For the case when the exchange time is very short, i.e. of the same order of magnitude or shorter than the rotational correlation times a further complication arises in the interpretation of relaxation times. These complications are considered in paper VIII where a general method of treating the problems is presented.

The basic idea in paper VIII is to introduce the chemical exchange in the hamiltonian in a semiclassical way by writing

$$H = \sum_i f_i(t) H_i \quad [8].$$

Here H_i is the hamiltonian characterizing site i . The function $f_i(t)$ takes the value unity if the nucleus under consideration is at site i at time t and zero otherwise. The hamiltonian in eq. [8] can be divided into a time independent and a time dependent part with zero mean value. It is the time dependent part that contributes to the relaxation, and this part of the

hamiltonian can be introduced into the standard derivations of relaxation rates (1) to obtain explicit expressions for the relaxation times.

The final expressions for the relaxation times depend on the detailed nature of the exchange process. It can, for example, be of importance to distinguish the case where the exchange occurs with complete retention of the magnitude and direction of the relaxation interaction (32) from the case when there is a complete randomization of the interaction on exchange (33). However, when one site is at a macromolecule and the other site has a very short rotational correlation time the two models give the same results as long as the exchange time is long compared to the shorter of the correlation times.

Fast intramolecular motions are often important when relaxation rates are considered. This can, for example, occur in the interpretation of nuclear Overhauser effects (34). Though not obvious from ref. 34, the calculation of an Overhauser effect reduces to a calculation of the contributions from the various dipole-dipole interactions to the total relaxation rate (1). Using the methods of section 2.3.4 of paper VIII the contribution of, for example, a fast rotating methyl group to the relaxation of another nucleus in the molecule can be calculated.

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1. The first part of the paper is devoted to the study of the

properties of the function $f(x)$ defined by the equation

$f(x) = \int_0^x f(t) dt$ and the function $g(x)$ defined by the equation

$g(x) = \int_0^x g(t) dt$ and the function $h(x)$ defined by the equation

$h(x) = \int_0^x h(t) dt$ and the function $k(x)$ defined by the equation

$k(x) = \int_0^x k(t) dt$ and the function $l(x)$ defined by the equation

$l(x) = \int_0^x l(t) dt$ and the function $m(x)$ defined by the equation

$m(x) = \int_0^x m(t) dt$ and the function $n(x)$ defined by the equation

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